ASEAN Journal for Science and Engineering in Materials

Journal homepage: https://ejournal.bumipublikasinusantara.id/index.php/ajsem

Graphene-Based Electrochemical Sensors for Heavy Metal Ions Detection: A Comprehensive Review

Muhammad Dilshad[1], Tariq Hussain[2], Shahbaz Ali[3], Muhammad Shakeel Shahzad[3], Muhammad Javed[4], Farhan Nazir Ahmad[5], Asaad Ahmad Zaki[6]*

[1]University of Punjab Lahore, Pakistan
[2]Government College University Faisalabad, Pakistan
[3]Khwaja Fareed University of Engineering and Information Technology, Rahim Yar Khan, Pakistan
[4]The Superior University, Lahore, Pakistan
[5]COMSATS University Islamabad, Lahore Campus, Pakistan
[6]University of Punjab, Pakistan
*Correspondence: E-mail: tariqhussain3132@gmail.com

ABSTRACT

The accumulation of heavy metallic ions in the human body causes serious damage. The tracking and removal of these ions is very necessary and that is done via electrochemical sensors because of quick response, high sensitivity, and low but large detection range. In this regard, the surface of the electrode plays a critical role in electrochemical performance. Here, we present a detailed review of work that has been done in the past to modify the surface of electrodes by testing the carbon nanoparticles i.e. graphene or graphene derivatives, and their combination with other nanoparticles. Mixing graphene or graphene oxide with other organic or inorganic materials forms nanocomposites which help to detect various kinds of heavy metal ions such as cadmium, mercury, copper, lead, zinc, etc. in tap water or food items. This review article includes the synthesis methodologies, working mechanisms, advantages, disadvantages, and future prospectus of this field.

ARTICLE INFO

Article History:
Submitted/Received 29 Jun 2024
First Revised 04 Aug 2024
Accepted 24 Oct 2024
First Available online 25 Oct 2024
Publication Date 01 Mar 2025

Keyword:
Electrochemical sensor,
Graphene-based,
Heavy metal.

1. INTRODUCTION

The concentration of heavy metal ions is increasing day by day due to various human activities, which is deteriorating the quality of environmental air and water. This exponential growth of heavy metal ions has threatened the health of all types of biological species via the food chain (Anwar *et al.*, 2020; Asif *et al.,* 2020; Akhtar *et al.,* 2020; Baghayeri *et al.,* 2019; Chen & Pei, 2020; Gao *et al.,* 2012). That's why, one should be careful about the existence of heavy metal ions in food or water, and for this purpose, researchers are developing ultrafast, reliable, and highly sensitive detection methodologies (Kim *et al.,* 2022; Lee *et al.,* 2016; Li *et al.,* 2018; Lin *et al.,* 2018; Lu *et al.,* 2018; Lu *et al.,* 2018), which would help out with food, water, and environmental safety (Asif *et al.,* 2021; Donald *et al.,* 2022; Asif *et al.,* 2024). There are some traditional methods for the detection of these ions such as chromatography (Nourbakhsh *et al.,* 2022; Pan *et al.,* 2021; Pang *et al.,* 2022; Punrat *et al.,* 2016; Rehman *et al.,* 2022), colorimetry, atomic spectrometry, and various others, but their detection accuracy is limited due to various reasons like high cost, experts, and troublesome pre-detection processing (Donald *et al.,* 2022; Asif, 2022; Asif *et al.,* 2022).

Modern electrochemical techniques help to measure and characterize the chemical as well as electrical responses of materials precisely (Nourbakhsh *et al.,* 2022; Pang *et al.,* 2022; Rehman *et al.,* 2022; Zhang *et al.,* 2022; Saisree *et al.,* 2023) that can be operated by renewable energy rather than conventional thermochemical processes (Asif *et al.,* 2023; Asif *et al.,* 2023; Hassan *et al.,* 2023; Ahmed *et al.,* 2024; Asif *et al.,* 2024). They are cost and user-friendly, small-sized apparatus, and fulfill the prerequisites of on-site detection. The dependence of the sensitivity of the electrochemical technique is on its front-end electrochemical type of sensor, which is the heart of this technique. So, for the fabrication of electrochemical sensors, researchers are looking for composite materials, that improve performance, sensitivity, stability, and lifetime effectively, however, the main important point is they are renewable and environmentally friendliness like other processes such as bio-energy, plastic waste degradation, and carbon recycling (Asif *et al.,* 2024; Kareem *et al.,* 2022; Yousuf *et al.,* 2022; Khan *et al.,* 2024). In this race, carbon nanomaterials are playing a crucial role in electrochemical reactions because of their excellent biocompatibility and high specific surface area. The high surface-to-volume ratio of carbon nanoparticles leads to enhanced surface reactivity, adsorptive capacity, surface-active potential capability, and catalytic efficacy. Comparing these carbon-based electrochemical sensors with other traditional sensors, they are smaller in size, have faster response rates, better reliability as well as high accuracy.

Likewise, carbon and graphene also have unique properties such as flexibility, carrier mobility, electrical conductivity, and high specific surface area. Pure graphene and its oxygenated products like graphene oxide (GO) and reduced graphene oxide (rGO), are considered potential candidates for biosensors (Zuo *et al.,* 2019). The oxygenated graphene has a high level of hydrophilicity, which makes it much more favorable for chemical reactions. One other big advantage of this class of materials (graphene, GO, and rGO) is that they are easy to combine with other inorganic nanoparticles (NPs) such as metal, metal NPs, metal oxides, semiconductor (SC) NPs, quantum dots (QDs), and organic biomolecular as well as polymers. This combination of graphene with other organic and inorganic NPs helps to fabricate the various types of graphene-assisted nanocomposites and these nanocomposites have high efficiency in biosensor-based applications. Nowadays, researchers are studying pure graphene and graphene-based materials and evaluating their electrochemical performance using various detection methods, as summarized in **Table 1**.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Table 1. Electrochemical heavy metal ions detection performance of graphene-modified electrodes.

Modified Electrodes	Technique	Metal Selectivity	Detection Limit	Linear Range	Reference
Bi/rGO/GCE	DPASV	Cadmium, lead	1.2, 0.2 µg /L	10-50 µg /L	(Khan *et al.*, 2024)
HTD@GO/GCE	SWASV	Chromium, copper	3.65, 2.25 µM	1-100 µM	(Kim *et al.*, 2022)
GQDTU-IIP	DPV, CV	Mercury	23.5 nM	5 . 10^{-8}, 2.3 . 10^{-5} M	(Soman *et al.*, 2021)
rGO.Co_3O_4.PEINCP	SWV, DNPV	Cd, Pb, Cu, Hg	1.069, 0.484, 0.285, 0.878, 2.398, 0.462, 1.115, 0.477 nM	-	(Rehman *et al.*, 2022)
GQD@VMSF	DPV	Hg, Cu, Cd	9.8, 8.3 pM, 4.3 nM	10 pM-1.0 nM, 10 pM-1.0 nM, 20 nM-1.0 μM	(Lu *et al.*, 2018)
Graphene/Chit-Fc/SPE	SWASV	Cd, Cu, Pb	0.5, 1, 5 µg /L	5-400, 2-200, 5-200 µg /L	(Liu *et al.*, 2018)
GO-PVA/SPE	DPV	Hg, Pb, Cd	0.0075, 0.015, 0.0312 ppb	0.0075-1 ppb	(Mishra *et al.*, 2017)
PA6/CNW:rGO	DPV	Hg	5.2 nM	2.5-200 µM	(Teodoro *et al.*, 2019)
PTh-afGQDs	CV, EIS	Hg	0.6 pM	1 pM-1 µM	(Tian *et al.*, 2020)
GO-AgNW	SWASV	Hg	0.10 nM	1-70 nM	(Rahman *et al.*, 2019)
SB@SiO_2@GO@ITO	SWASV	As	156 pM	0.150-0.930 nM	(Kaur *et al.*, 2019)
rGO/Fe_3O_4	SWASV	As	0.12 ppb	0.01-5050 ppb	(Devi *et al.*, 2017)
rGO, tetraphenylporphyrin	DPV	Cd	0.022 mM	0.05-300 mM	(Si *et al.*, 2018)
AuNPs/3D rGO	DPadSV	Cr	1.16 µg /L	25-300 µg /L	(Xu *et al.*, 2019)
PANI/GQD	LSCV	Cr	0.097 mg /L	0.1-10 mg /L	(Punrat *et al.*, 2016)
PVA/chitosan-TRG	SWASV	Lead	0.05 ppb	1-50 ppb	(Nguyen *et al.*, 2021)
Bi/Naflon/rGO-GNPs	SWASV	Lead, cadmium	0.08, 0.12 mg /L	1-90 mg /L	(Zhao *et al.*, 2017)
PrGO/AuNPs/Sal-Cy	SWASV	Cadmium, Lead	0.06, 0.04 nM	1-10 nM	(Priya *et al.*, 2019)
N@LEG	SWASV	Cadmium, lead	1.08, 0.16 g /L	5-380, 0.5-380 g /L	(Lin *et al.*, 2018)
GO-PVA	DPV	Hg, Pb, Cd	7500, 15000, 31200 ng /L	7500-10000 ng /L	(Akhtar *et al.*, 2020)
rGO/Ala/PANI	SWASV	Cd, Pb, Cu	0.03, 0.045, 0.063 nM	100-0.08 nM	(Zhu *et al.*, 2014)

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Keeping in view the detection methods, we have reviewed the synthesis methodologies, working mechanisms, and electrical performance of electrochemical sensors fabricated with pure graphene and its oxygenated derivatives. This work would be helpful for researchers by engaging them to literature, current scenarios, and future responses of the electrochemical detection field.

2. METHODS

This study is a literature, in which data was collected and compiled from internet sources (especially articles published in international journals). Data was analyzed and summarized to make this article.

We used several abbreviations: Cyclic voltammetry (CV), Differential pulse voltammetry (DPV), Graphene oxide (GO), Indium tin oxide (ITO), Square wave anodic stripping voltammetry (SWASV), differential pulse anodic stripping voltammetry (DPASV), Glassy carbon electrode (GCE), signal-noise ratio (SNR), Square wave voltammetry (SWV), Reduced graphene oxide (rGO), Limit of detection (LOD), Screen printed electrode (SPE), Nanoparticles (NPs), Carbon nanotubes (CNTs), fluorinated multi-walled carbon nanotube (FMWCNT), Ferrocene carboxylic acid functionalized metal-organic framework (Fc-NH2-UiO-66), Graphene aerogel (GA).

3. RESULTS AND DISCUSSION

3.1. Graphene-based electrochemical sensors

The performance and progress of electrodes have been raised with the help of graphene. The composite of gold and cysteine NPs (Au-GN-Cys) was prepared to explore the activeness of surface, enlargement, and better electrical and chemical activity of graphene (Thiruppathi *et al.,* 2017). Ultrasonic treatment and quick agitation were done to get the uniform Au-GN-Cys dispersion, and then by using the evaporation deposition method, the sample was modified on a bismuth film glassy carbon electrode. The SWASV response of the above-mentioned composite, GCE, and Au-GN/GCE in situ plating bismuth thin films for lead and cadmium detection. The Au-GN/GCE shows a high ion detection response among other samples because of its good electrical conductivity and high surface area of graphene. There is another reason behind its high ion detection ability and that is the synergetic effect of Au-GN and cysteine on metal deposition and it offers a big opportunity to detect Pb and Cd in an aqueous solution.

Here, the doping phenomenon retains the original properties of graphene as well as maintains the properties of composite materials. In this regard, the effort was made to synthesize fluoride GO (FGO) materials by a one-pot method utilizing doping and functionalization to boost the electrochemical response of pure and graphene-based materials (Lee *et al.,* 2016). The characteristic response of this material declared the increasing trend for capacitance than GO material. The core reason behind its increasing capacitance is the presence of a layered structure of 1% F, which boosted its electrochemical detection and stability. **Figures 1 (a-c)** show the characteristics, features, and results regarding the detection of FGO.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

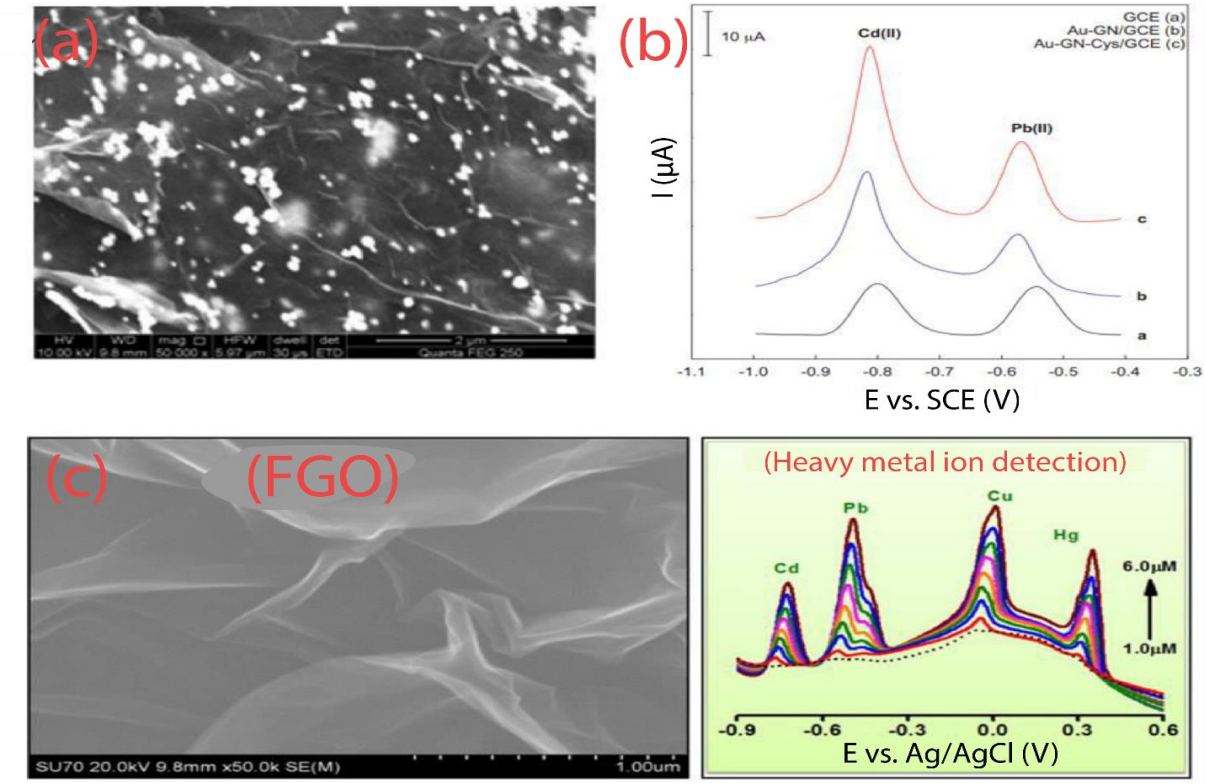

Figure 1. (a) SEM images, (b) SWASV curves, (c) Characterization and detection results (Zhu *et al.,* 2014; Thiruppathi *et al.,* 2017)

Similarly, graphene-based metal or metal oxide NPs have large surface-to-volume ratio and high adsorption capacity, and they have good performance while being used in electrochemical sensors. Using a simple solve-free thermal decomposition technique, Piao et al. synthesized iron oxide (Fe2O3) NPs and then mixed these NPs with graphene to fabricate electrochemical-based heavy metal ion detectors (Cui *et al.,* 2015). This modified electrode showed excellent performance for heavy metal ion detection because of the synergistic relation between Fe2O3 NPs and graphene. Within the optimized conditions, zinc, cadmium, and lead electrodes had a linear range of 1-100 µg /L while their detection limits were 0.11, 0.08, and 0.07 µg /L, respectively (SNR=3). Moreover, Cui *et al.* (2015) synthesized bismuth NPs (BNPs) rich nanoporous carbon on graphene sheets by pyrolytic deposition method. The characteristic response of this sample for anodic stripping voltammetry heavy ion detection was observed excellent due to large pore size, high surface area, and excellent electrical conductivity. Within the optimized environment, the BNP-rich nanoporous carbon electrode can detect cadmium and lead simultaneously in limits of 4.1 and 3.2 nM, respectively.

Additionally, graphene derivatives are being utilized for the formation of functionalized materials which facilitate the cluster formation of heavy metallic ions. Gong *et al.* (2014) prepared the GO sample by mixing hydroxyl with epoxide, which aided in the functionalization of graphene samples via surficial covalent bond modification. A thorough guide about electrode working and its ion detection performance is shown in **Figures 2(a and b)**. A coupling technique was followed assisted by ethyl carbodiimide/N-hydroxy succinimide (EDC/NHS) to connect the edge of GO with the top surface of an L-cysteine-based Au electrode, and this fabricated detector has an ultra-sensitive detection effect and LOD for metallic ions is 0.4, 0.8 and 1.2 for Pb, Hg, and Cu, respectively. Thus, to boost the detection capability of heavy ions, the inconclusion of special and unique structures is essential. For this purpose, Gao *et al.* (2012) fabricated the Au electrodes having the 3D nanoporous structures

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

by adopting the ion beam sputtering technique to sputter the argon ions on the glass base layer, as shown in **Figure 2c** (Gao *et al.,* 2012). The presence of nanoporous structures improved the detection range and accuracy, where the range of detection of copper and lead is 0.009-4 and 0.006-2.5 µM, respectively. Finally, excellent stability, good reusability, and great anti-interference capability were demonstrated by these electrodes.

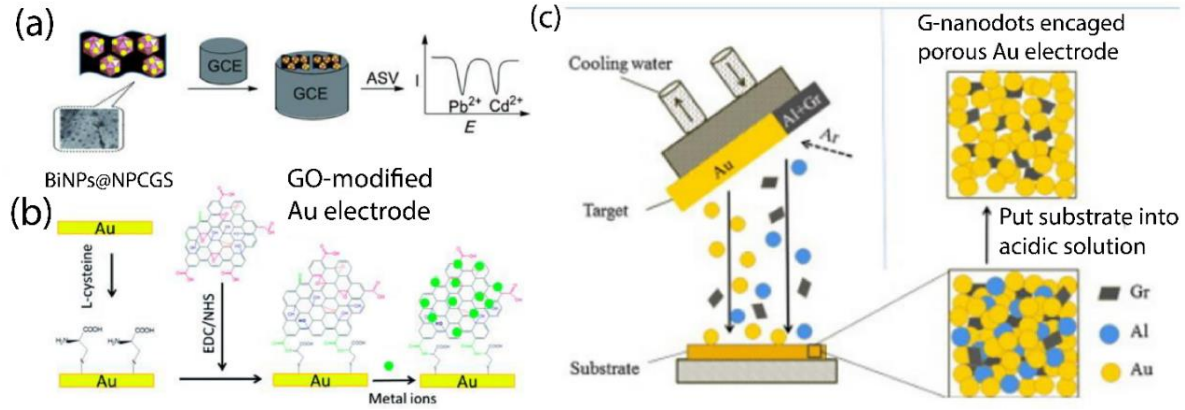

Figure 2. (a) Schematic illustration of material composites, (b) Schematic illustration of sensor synthesis, (c) Schematic illustration of porous electrode (Cui *et al.,* 2015; Gong *et al.,* 2014; Zhu *et al.,* 2015)

Recently, the electrodes fabricated by graphene or its derivatives such as graphene nanoplates, sheets, quantum dots, and fluorinated graphene have been studied due to surface modification and excellent performance in heavy metallic ionic species detection. In this regard, Srivastava *et al.* (2020) studied the sensor fabricated by graphene monolayers for heavy metallic ions detection in water. Nourbakhsh *et al.* (2022) studied the detection of lead, cadmium, and copper in tap water by depositing the Ag nanoparticles on the surface of graphene nanoplates.

3.2. rGO-modified electrochemical sensors

The oxygen-containing functional group is removed via the reduction of GO to form the rGO, and this product has structural defects at a large scale, and its performance is dependent upon the reduction methods that are being used. The synthesis process of rGO is quite easy and that's why it is been used in the electrochemical detector's field. Moreover, many researchers have studied the impact of reduction methods on electrochemical detector performance. In this respect, Xuan *et al.* (2019) synthesized the rGO by inducing the glucose to the hydrothermal process of rGO, and then to fabricate the electrochemical detector for Au electrodes, modified Bi was deposited on the surface of rGO. For this detector, the linear detection range was found 1-100 g /L for both ions, and for lead and cadmium, these were 0.4 and 1 g /L (SNR=3), respectively.

In the same way, Al-Gahouari *et al.* (2021) explored the impact of the electrochemical reduction method on a modified electrode for its heavy metal ions sensing performance, as shown in **Figure 3**. An improved hummers technique was followed to prepare the GO and then coating was done on three substrates ITO, copper, and GCE, for surface analysis, electrochemical analysis, and sensing performance, respectively. rGO films were prepared by adopting different reduction methodologies, and then associated characterization was performed such as CV, UV-visible spectroscopy, XRD, AFM, FESEM, and attenuated total reflectance-infrared spectroscopy. These analysis reports demonstrate the organization's structural details having different reduction methods for rGO. CV measurements have shown

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

this sample as the best detector for heavy metallic ions, and the detection range for cadmium and lead was found 1.2 and 0.2 µg /L, respectively.

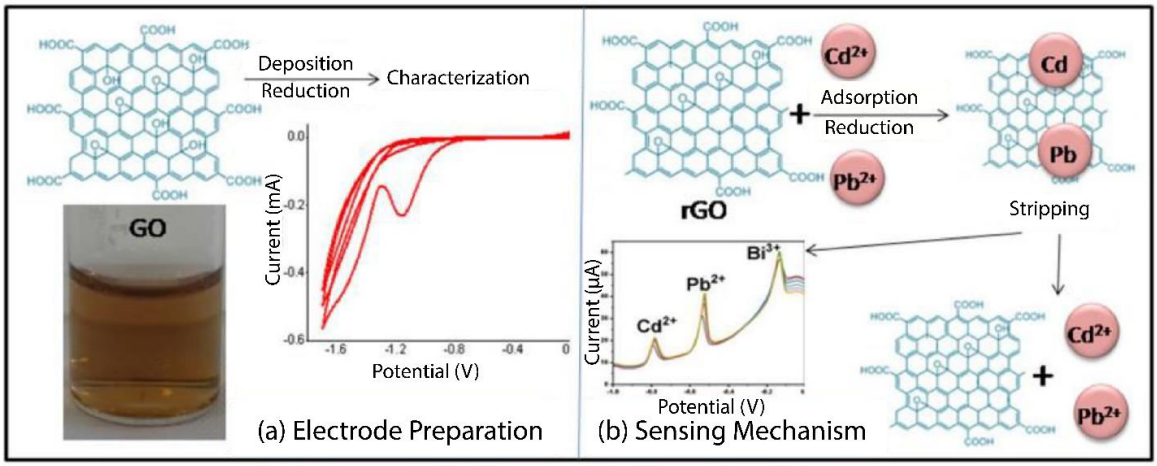

Figure 3. Schematic illustration of heavy metal ion detection at different degrees of reduction

Metallic NPs are considered as high surface-to-volume ratio NPs and show excellent catalytic activity as well as better electrochemical detection performance when combined with rGO. For this purpose, Fei et al. synthesized the TiO2/rGO composites following the hydrothermal technique where the reduction of GO and TiO2 happened simultaneously to shorten the reaction steps, as shown in **Figure 4** (Vajedi & Dehghani, 2019). The adsorption capacity of these composites was explored for heavy metallic ions in the aqueous solution as well as probed its detection capacity in glassy carbon electrodes using SWASV. The composites showed remarkable electrochemical sensing performance for trace amounts as well as for the removal of heavy ions due to stable chemical properties and effective adsorption capacity of nanocomposites. Likewise, Kumar *et al.* (2017) prepared the nanocomposites of rGO and nickel tungstate (rGO/NiWO4) using the hydrothermal technique and found the binary metal oxide NPs. These NPs helped to reduce the restacking of graphene layers are spacers and boosted the electrochemical sensing performance as catalysts. To measure the electrochemical activity, DPASV was utilized and LOD of cadmium, lead, copper, and mercury was found to be 4.7. 10-10, 3.8. 10-10, 4.4. 10-10, and 2.8. 10-10 M, respectively. Further, these composites were found to be the best candidates for membrane filtration. In this regard, hydrothermal and vacuum filtration was used to synthesize the rGO composites where to reduce the aggregation of surficial ZnO ultrasonic treatment of ethylenediamine tetraacetic acid (EDTA) was done. This ultrasonic treatment further increased the surface area and boosted the heavy metallic ion detection capacity. The maximum detection range for cadmium, lead, copper, and mercury was found to be 5.6, 6.8, 2.5, and 1.0 µM, respectively, and maximum adsorption performance was declared as 2963, 8056, 600, and 1753 mg/g, respectively.

A large number of oxygenated functional groups are present in amino acids which help in the adsorption of heavy metallic ions and that's why researchers are exploring the composites of amino acids and rGO. In this regard, Wei *et al.* (2019) observed the carboxyl group that promotes the combination of PGA and heavy metallic ions, and then for material modification, they induced the porphyrin into PGA as a terminal group. The conjugated type ring structural shape of porphyrins has static interactions with the conductive samples such as carbon nanotubes or graphene to boost the detection performance of metallic ions, as shown in **Figure 5a**. The observed detection limits for cadmium, copper, and mercury were as

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

0.015, 0.024, and 0.032 µm, respectively. Similarly, Akhtar *et al.* (2020) synthesized the detector by combining alanine and polyaniline with graphene samples to fabricate the sensor (rGO/Ala/PANI/GCE), as shown in **Figure 5b**. The synergic complexation properties and good chelation affinity of metals and alanine modified the effective surface-to-volume ratio and boosted the selectivity, stability, and sensitivity of electrochemical sensors. Under optimized conditions, the electrochemical detection performance of cadmium, lead, and copper was found excellent in aqueous solutions.

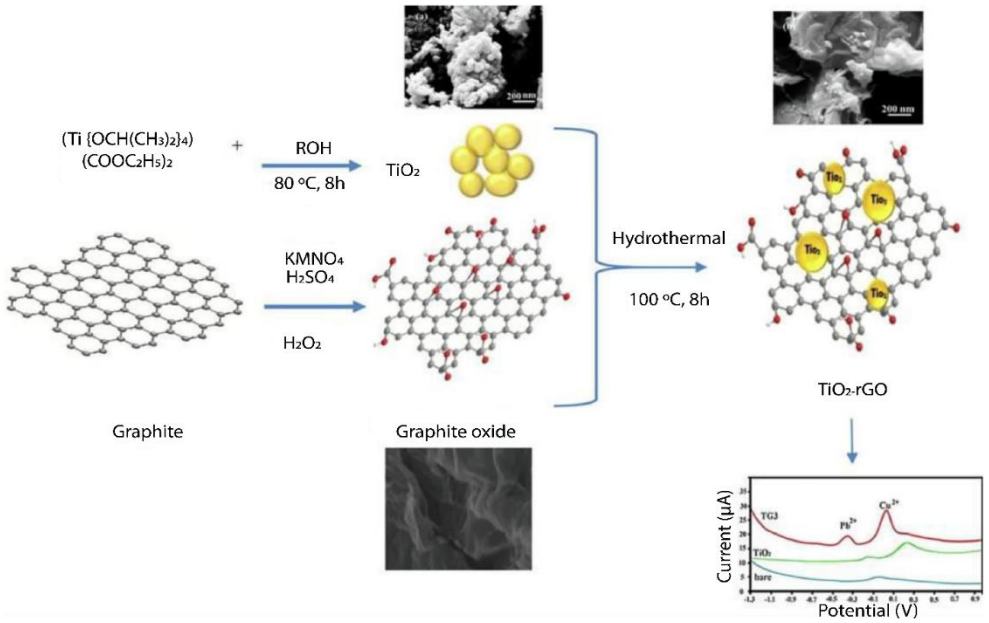

Figure 4. Schematic illustration of nanocomposite formation (Vajedi & Dehghani, 2019)

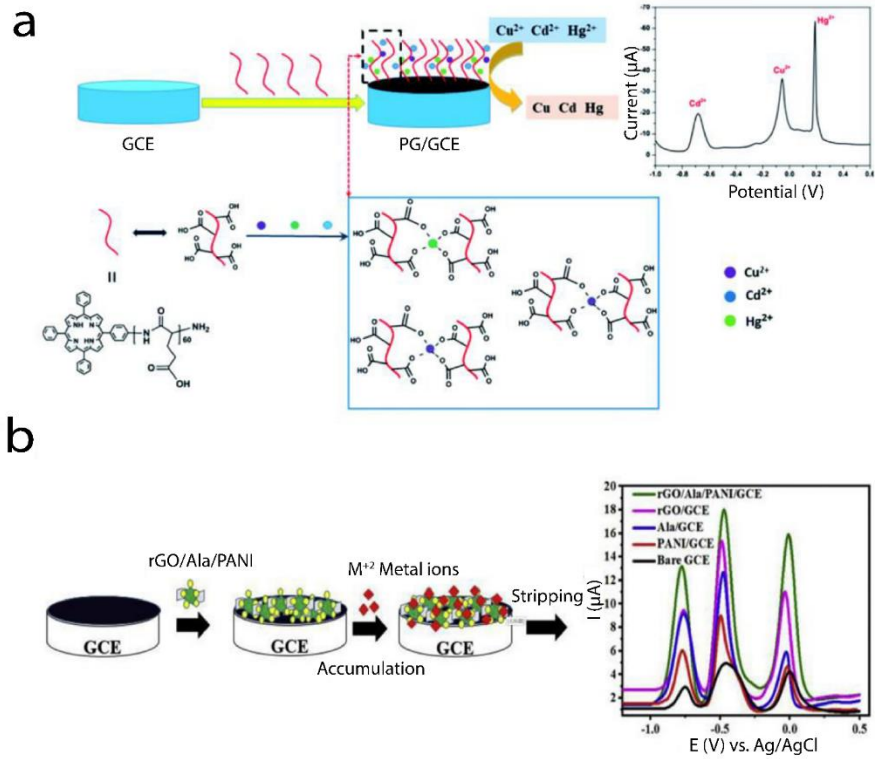

Figure 5. (a) Schematic illustration of PGA and rGO-based electrode for heavy metal ions detection, (b) rGO/Ala/PANI/GCE-based electrode synthesis (Akhtar *et al.*, 2020; Yi *et al.*, 2019)

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

To enhance electrochemical performance, the modification of other functional groups on rGO is considered also important. For this purpose, Pang *et al.* (2022) followed the hydrothermal calcination method to synthesize the NCO/N and S-RGO composites and found remarkable electrochemical detection activity, as shown in **Figure 6a**. Additionally, some structural defects have been created in composites by the SNR atoms doping and these sulfur-based functional groups lowered the transmission resistance, boosted the wettability of electrochemical electrodes, and enhanced the efficacy of electroactive diffusion. These composite-based carbon electrodes showed remarkable detection efficiency of heavy metal ions, excellent stability, high anti-interference, and good reproducibility, as shown in **Figure 6b**. Other than this, Si *et al.* (2018) synthesized furfural/rGO composites by furfural in situ on rGO to raise the detection ability because of oxygenated content on the surface which provides the huge sites for metal ions. Additionally, this composite itself showed low electrical resistance and a high surface-to-volume ratio which enabled the coordination of heavy metallic ions excessively. The carbon electrode modified by this composite has good selectivity, excellent stability, and remarkable detection performance from 93% to 105% for cadmium, lead, copper, and mercury.

The outer or inner surface of organic covalent frame materials has abundant cavity structures, voids, particle gaps, and porous channels, which enhance the catalysis performance in electrochemical reactions. For this purpose, Pan *et al.* (2021) synthesized an intercalated composite that contained the graphene and hydro-sulfonyl functional organic covalent framework. This sample has having fine fibrous structure and offers several active positions and larger electroactive sites are created due to graphene involvement. So, a better channel for electron movement has been projected between a deposited sample and the electrode substrate. In return, the fabricated electrochemical detector made by this composite had a high degree of determination of heavy metal ions and 0.3, 0.2, 0.2, and 1.1 µg /L were recorded for cadmium, lead, copper, and mercury, respectively under optimized parameters. The detection ability was observed to be dependent on the special material structures. Shi *et al.* (2017) followed the chemical reduction method to synthesize the 3D porous graphene material to disperse bismuth NPs which accumulated on the electrode surface due to the reduction phenomenon, as shown in Figure 6b. Because of the large specific surface area, quick electron transportation, and remarkable structural stability, this 3D graphene-assisted Bi NPs electrode has excellent ability for heavy metal detection.

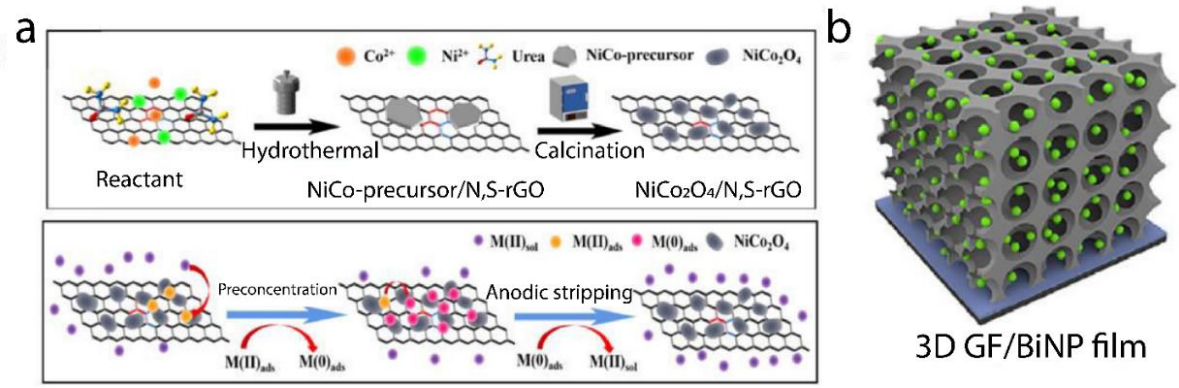

Figure 6. (a) Schematic illustration of the heavy metal ion detection process, (b) 3D illustration of graphene/bismuth NPs film (Pang *et al.*, 2022; Xu *et al.*, 2021)

Another class of materials i.e. conjugated organic semiconductors, have fast signal transduction, high conductivity, and customized charge transfer properties. The sensitivity and selectivity are been improved due to redox direct interaction with the analyte via pi-

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

conjugation. So, a combination of this semiconductor and carbon nanotubes enhances the electrochemical detection performance. In this regard, Kim *et al.* (2022) utilized the Suzuki coupling mechanism synthesized the diketone oligomer, and then prepared the solution of GO and oligomer and fabricated casting on GCE. Furthermore, this sample was utilized for chromium and copper detection, as shown in **Figure 7**. The uniform and homogenous dispersion of the solution was obtained, and good bonding was observed. The large specific surface area promoted the electron transfer rate and enhanced the selectivity and sensitivity of the detector. A strong anodic current was observed for the above-mentioned ions and detection limits at optimized conditions were observed as 3.65 and 2.25 µM, respectively.

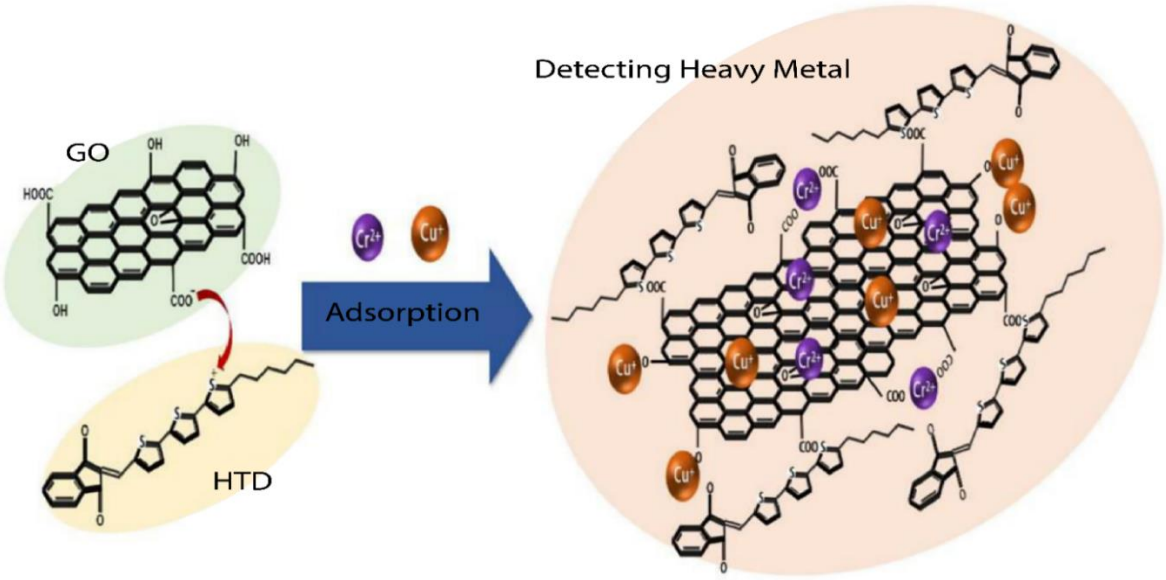

Figure 7. Schematic illustration of detection of chromium and copper ions (Kim *et al.,* 2022)

3.3. Graphene quantum dots-based electrochemical detector

Generally, the direct use of graphene enhances the electrochemical performance of electrodes and for this purpose, researchers are trying to fabricate graphene aerosols, and quantum dots for electrochemical sensor fabrication. 0D or graphene quantum dots have planar carbon structures, and they are being used in different applications because of their high specific surficial area, tunable physicochemical characteristics, high molecular size, good solubility, good biocompatibility, and fluorescence characteristics. High sensitivity and high detection performance were observed in fluorescence detectors fabricated by graphene quantum dots. For this purpose, gold NPs and novel conjugates of graphene quantum dots for heavy metallic ions detection in the electrochemical detector and detection limits were observed as 0.02 and 0.05 nM for mercury and copper, respectively.

The bottom-up technique was followed by Chen and Pei (2020) prepared the graphene quantum dots to prove the surface state and size of graphene quantum dots. Furthermore, they synthesized mesoporous silica membranes associated with indium tin oxide electrodes following the Stober solution growth technique. An electrochemical deposition method was observed to deposit the graphene quantum dots inside the nanochannel. CV measurements helped to understand the fact that there was no hindered mass transfer in the nanochannel due to graphene quantum dots deposition although they favor enhancement of positively charged analytes. So, to not the composition in the complex samples, they utilized this electrochemical detector based on reduction and electrodeposition of metallic ions and anodic stripping by DPV. Different functional groups were fabricated along with graphene

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

quantum dots for electrode fabrication by adopting the electrochemical method. The electrostatic interaction of graphene quantum dots is the core reason to improve the detection range such as 9.8, 8.3, and 4.3 nM for mercury, copper, and cadmium, respectively, as shown in **Figure 8**. The good combination of graphene quantum dots and functional groups enhances the linearity and performance for analyzing the concentration in the sample.

Graphene quantum dots-based sensors are considered economical and simple synthesis methodology and are helpful to boost the electrochemical performance of these sensors. For this purpose, Lu *et al.* (2018) confined the graphene quantum dots in nanochannels of vertical sites of mesoporous silica-nanochannel layers via electrophoresis for heavy metal detection of mercury in seafood. Here, antifouling and anti-interference characteristics were demonstrated via steric exclusion and electrostatic repulsion due to the presence of silica-nanochannel layers. The abilities of recognition elements and signal amplifiers were observed for quantum dots, and they interacted with analytes to get the nanoconfined abundance and promoted the charge transfer activity which ultimately enhanced the sensitivity and selectivity for analytes. The detection linear range was observed as 10 pM-1.0 nM, 20.0 nM-1.0 µM, and 10 pM-1.0 nM for copper, cadmium, and mercury, respectively.

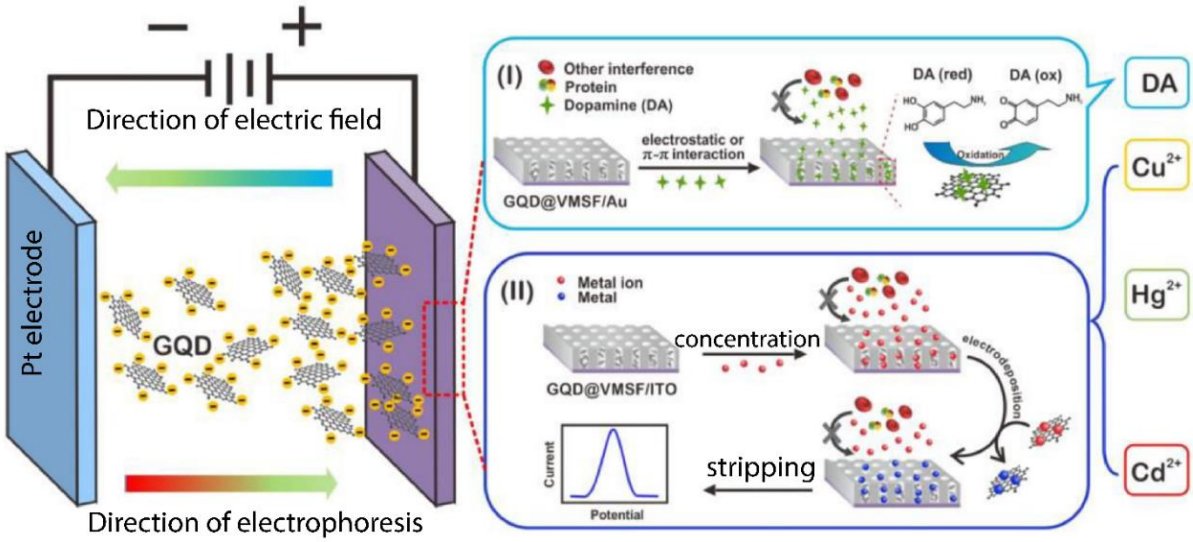

Figure 8. Schematic illustration of electrode synthesis for heavy metal ions detection (Lu *et al.,* 2018)

The intrinsic characteristics of graphene quantum dots were tuned by the induction of heteroatoms such as chemical, electronic, and catalytic properties. In this regard, Saisree *et al.* (2023) followed the facile hydrothermal technique to prepare the S, N-graphene quantum dots for the detection of cadmium, lead, and mercury. There was no need for extra pre-deposition treatment for stripping analysis in electrode synthesis since these electrodes show the ability to spontaneously lower heavy metal ions to zero valence state. The introduction of S boosted the conductivity and electrocatalytic behavior by squeezing the band gap because of electronegativity. The excellent detection limits for this electrode were found as 10-12, 10-11, and 10-12 M, while electrochemical sensitivity performance was obtained as 5, 13, and 12 $\mu A \mu M^{-1} cm^{-2}$ for mercury, lead, and cadmium, respectively.

3.4. Graphene aerogels based electrochemical detectors

At the macroscopic scale, graphene aerogels demonstrate exceptional characteristics such as mechanical strength, electrical or thermal conductivity, porosity, and large surface-to-

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

volume ratio due to their uniform porous structure or network assembly. In this respect, the hydrothermal method was adopted by Chen and Pei (2020) to synthesize the graphene aerogels and metal-organic framework following the self-assembly process. It has a higher specific surface area and porosity than its traditional porous materials. N, N-dimethylformamide (DMF), water, and ethanol can be separated following the heat treatment method during the synthesis of this framework to form the coordination of unsaturated metal ions which then serve for substrate reaction as an active site. Secondly, the involvement of special types of functional groups made this framework more active in catalytic reactions which can be induced by choosing ligands having two functional groups or following the post-synthetic modification. The evaporation deposition technique was followed to modify the glassy carbon electrode for electrochemical detection activity and found excellent performance due to the synergetic effect of aerogels and its high surface area and conductivity, as shown in **Figure 9**. The detection limits of the electrochemical sensor were obtained as 0.02, 1.5, 7, and 2 nM for cadmium, lead, copper, and mercury, respectively.

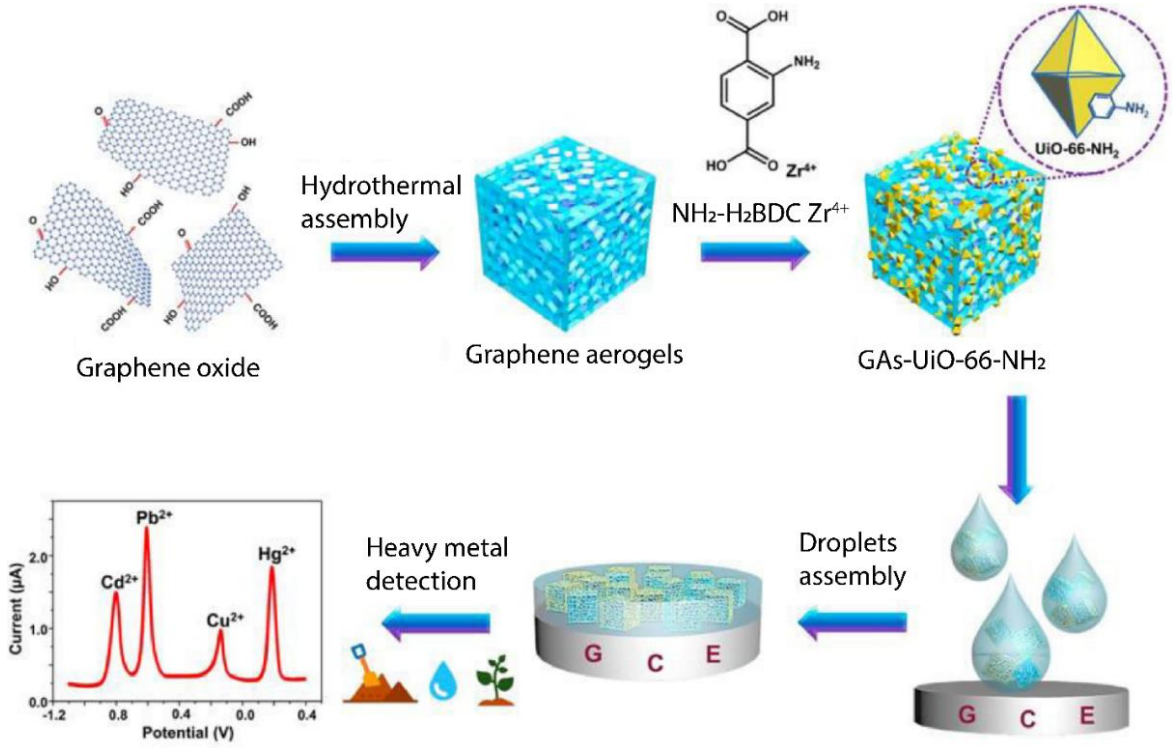

Figure 9. Schematic illustration of composite synthesis for electrode material (Lu *et al.,* 2018)

3.5. Graphene-noble metals modified electrochemical sensors

The combination of noble metals (normally gold, silver, platinum, and palladium) and graphene enhances characteristics such as stability, conductivity, catalytic activity, specific surface area, and reproducibility. This combination not only raises the properties but also boosts the anti-aggregation nature of graphene oxide sheets. Due to these synergistic effects of the combination of NPs, the detectors have ultrahigh sensitivity for the detection of heavy metallic ions. For this purpose, Zhao *et al.* (2020) followed the one-pot homogenous precipitation technique to synthesize the GO and Ag2S composite to detect mercury. The juice samples have been analyzed and real environmental water and got a relative standard deviation below 5.5%.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Similarly, Rahman *et al.* (2019) fabricated the sensor using the GO and Ag nanocomposite and used SWASV to detect the mercury in tap water. The -COOH functional group present on the GO surface deoxidized the mercury ion due to the high standard reduction potential. Thus, in the presence of interferents, the sensor demonstrated excellent selectivity for mercury and boosted the conductivity of GO because of its high conductivity. The AgNWs overlapping enables the electron conduction pathway via GO sheets which is compensated for smaller electrical conductivity of GO. The detection linear range was obtained as 1-70 nm along with a sensitivity of 0.29 µA/nM and declared as the best choice for mercury detection in tap water.

Ferrite NPs have excellent conductivity, electrochemical activity, high specific surface area, and good adsorption capability and are localized on the magnetized glassy carbon electrode. Zhang *et al.* (2022) combined the Fe_3O_4 NPs with GO to enhance the selectivity, sensitivity, and adsorption capacity for heavy metallic ion detection. Similarly, Baghayeri *et al.* (2019) followed the SWASV technique to fabricate the electrochemical sensor based on amidoamine dendrimer for tracing lead and cadmium in river and lake water. A rough surface was noted due to uniform aggregation of Fe3O4 NPs on the nanosheets of GO where dendrimer molecules offered a high degree of aggregation. The exceptional properties of GO and synergistic effects of the adsorption capacity of Fe3O4 boosted the detection performance ranging from 0.2-140 µg /L and 0.4-120 µg /L for cadmium and lead, respectively.

3.6. Graphene with non-metallic NPs for sensor fabrication

GO can be combined with metal NPs but they are being combined with non-metal NPs such as nitrogen-doped carbon QDs or some other organics. This combination modifies the interactions for the detection of heavy ions. In this regard, Li *et al.* (2018) presented an electrochemical setup that was fabricated with GO and nitrogen-doped QDS for cadmium and lead detection in tap and lake water using the anodic stripping voltammetry technique, as shown in **Figures 10(a-d)**. Here, stripping peaks were produced due to the re-oxidization of zero-valent metals to metallic ionic species due to nitrogen doping. GO was serving as a carrier to load the nitrogen-doped QDs, which ultimately increased the electron transfer rate as well as the conductivity of the sample. They provided various oxygenated functional groups on surfaces and were working as anchor sites along with cadmium which led to a boost in the analysis performance. The sensor showed remarkable performance due to QDs and GO and found the linear detection range 20.72-10360 and 11.24-11241 µg /L for lead and cadmium, respectively. Additionally, the sensor showed good anti-interference properties for interfering metallic ions.

Similarly, Jayaraman *et al.* (2022) fabricated another sensor for chromium and mercury detection, that was based on covalently dual functionalized graphene oxide. An epoxide ring cleavage and simultaneous reduction were followed to prepare the thymine-GO-carbohydrates, and this sample can induce stronger interactive forces with mercury and chromium. Thus, the fabricated sensor proposed excellent properties such as stability, sensitivity, reusability, and selectivity for mercury and chromium due to the advantages of organic and inorganic species. On the other hand, Wei *et al.* (2019) proposed the chitosan-GO composites polymer for the detection of copper in river and tap water selectively. The rough surface of this polymer is helpful for the enrichment of copper and the sensor demonstrated a large detection range of 0.5-100 µM, excellent selectivity for copper, and a very low detection limit of ~ 0.15 µM.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

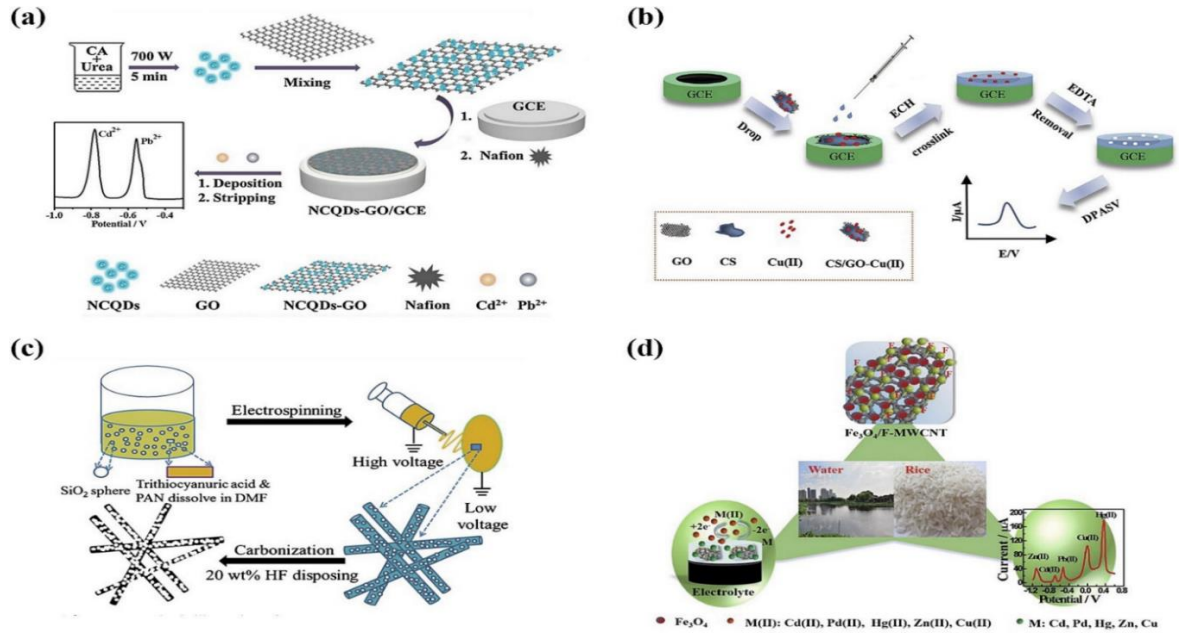

Figure 10. (a) Schematic illustration of NCQD-GO-GCE electrochemical sensor, (b) CS/GO-IIP sensor, (c) Schematic diagram of N, S-PCNF, (d) Layout and detection mechanism of the sensor (Li *et al.,* 2018; Wei *et al.,* 2019; Gao *et al.,* 2018; Wu *et al.,* 2019)

4. CONCLUSION

The relatively low concentration of heavy metallic ions is crucial to detect but they are highly toxic and have serious impacts on human life as well as environmental conditions. With the rise in the industry of nanocomposites, the detection of heavy metallic ions is also improved by the modification of electrodes with nanomaterials. The electrode surface is very important which will decide the electrochemical performance and detection range, so their surfaces are modified with nanomaterials. Carbon nanoparticles, graphene, or its derivatives have remarkable electrical properties due to their chemical structure and are being used for the fabrication of electrochemical sensors. Nowadays, new materials such as graphene aerogels, and quantum dots are combined with other organic, inorganic, metal, or non-metal nanoparticles to improve electrochemical performance. There are some challenges like an aggregation of magnetic materials, low conductivity of graphene oxide, or the insolubility of metal-organic framework in an aqueous medium. So, a new class of nanocomposite materials is needed which will express both electrical and magnetic response best. Researchers must look at materials with long reproducibility, stability, and excellent electrochemical properties.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

6. REFERENCES

Ahmed, S., Bibi, S.S., Irshad, M., Asif, M., Khan, M.K., and Kim, J. (2024). Synthesis of long-chain paraffins over bimetallic Na–Fe0. 9Mg0. 1Ox by direct CO2 hydrogenation. *Topics in Catalysis, 67*, 363-376. 2024.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Akhtar, M., Tahir, A., Zulfiqar, S., Hanif, F., Warsi, M.F., Agboola, P.O., and Shakir, I. (2020). Ternary hybrid of polyaniline-alanine-reduced graphene oxide for electrochemical sensing of heavy metal ions. *Synthetic Metals, 265*, 116410.

AL-Gahouari, T., Sayyad, P., Bodkhe, G., Ingle, N., Mahadik, M., Shirsat, S., and Shirsat, M. (2021). Controlling reduction degree of graphene oxide-based electrode for improving the sensing performance toward heavy metal ions. *Applied Physics A, 127*, 1-16.

Anwar, S., Sharf, B., Usman, M., Panday, D., and Asif, M. (2020). Organic diet as silent pretreatment strategy to boost immune system against SARS-CoV-2. *AlQalam Journal of Medical and Applied Sciences,* 3(2), 10-25.

Asif, M. (2022). Comparative study on extraction of humic acid from Pakistani coal samples by oxidizing the samples with hydrogen peroxide. *ASEAN Journal of Science and Engineering, 2*(1), 1-8.

Asif, M., Bibi, S.S., Ahmed, S., Irshad, M., Hussain, M.S., Zeb, H., Khan, M.K., and Kim, J. (2023). Recent advances in green hydrogen production, storage and commercial-scale use via catalytic ammonia cracking. *Chemical Engineering Journal, 473*, 145381.

Asif, M., Hussain, M.A., Riaz, A., Mujahid, R., Akram, M.S., Haider, B., Kanwal, S., and Zeb, H. (2023). A physical coal cleaning approach for clean energy production from low grade Lakhra coal of Pakistan using diester table. *Journal of the Pakistan Institute of Chemical Engineers, 51*(2), 1-9.

Asif, M., Saleem, S., Tariq, A., Usman, M., and Haq, R.A.U. (2021). Pollutant emissions from brick kilns and their effects on climate change and agriculture. *ASEAN Journal of Science and Engineering, 1*(2), 135-140.

Asif, M., Salman, M.U., Anwar, S., Gul, M., and Aslam, R. (2022). Renewable and non-renewable energy resources of Pakistan and their applicability under the current scenario in Pakistan. *OPEC Energy Review, 46*(3), 310-339.

Asif, M., Shafiq, M., Imtiaz, F., Ahmed, S., Alazba, A.A., Hussain, H.N., Butt, F.N., Zainab, S.A., Khan, M.K., and Bilal, M. (2024). Photocatalytic degradation of methyl orange from aqueous solution using ZnO by response surface methodology. *Topics in Catalysis, 67*, 1-9.

Asif, M., Sharf, B., and Anwar, S. (2020). Effect of heavy metals emissions on ecosystem of Pakistan. *Indonesian Journal of Social and Environmental Issues (IJSEI), 1*(3), 160-173.

Baghayeri, M., Alinezhad, H., Fayazi, M., Tarahomi, M., Ghanei-Motlagh, R., and Maleki, B. (2019). A novel electrochemical sensor based on a glassy carbon electrode modified with dendrimer functionalized magnetic graphene oxide for simultaneous determination of trace Pb (II) and Cd (II). *Electrochimica Acta, 312*, 80-88.

Chen, X., and Pei, Y. (2020). Application of graphene-based nanocomposites in electrochemical detection of heavy metal ions. *Science of Advanced Materials, 12*(3), 435-440.

Cui, L., Wu, J., and Ju, H. (2015). Synthesis of bismuth-nanoparticle-enriched nanoporous carbon on graphene for efficient electrochemical analysis of heavy-metal ions. *Chemistry–A European Journal, 21*(32), 11525-11530.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Devi, P., Sharma, C., Kumar, P., Kumar, M., Bansod, B.K.S., Nayak, M.K., and Singla, M.L. (2017). Selective electrochemical sensing for arsenite using rGO/Fe3O4 nanocomposites. *Journal of Hazardous Materials, 322*, 85-94.

Donald, A.N., Asif, M., and Felicien, S. (2022). A review on the centralised municipal sewage and wastewater treatment unit processes. *MOJ Ecology & Environmental Sciences, 7*(2), 31-38.

Gao, C., Yu, X.Y., Xu, R.X., Liu, J.H., and Huang, X.J. (2012). AlOOH-reduced graphene oxide nanocomposites: one-pot hydrothermal synthesis and their enhanced electrochemical activity for heavy metal ions*. ACS applied materials & interfaces, 4*(9), 4672-4682.

Gao, S., Liu, J., Luo, J., Mamat. X., Sambasivam, S., Li, Y., Hu, X., Wågberg, T., and Hu, G. (2018). Selective voltammetric Cd(II) determination using N,S-codoped porous carbon nanofibers. *Microchimica Acta, 185*, 282.

Gong, X., Bi, Y., Zhao, Y., Liu, G., and Teoh, W.Y. (2014). Graphene oxide-based electrochemical sensor: A platform for ultrasensitive detection of heavy metal ions. *RSC Advances, 4*(47), 24653-24657.

Hassan, A.M.M., Asif, M., Al-Mansur, M.A., Uddin, M.R., Alsufyani, S.J., Yasmin, F., and Khandaker, M.U. (2023). Characterization of municipal solid waste for effective utilization as an alternative source for clean energy production. *Journal of Radiation Research and Applied Sciences, 16*(4), 100683.

Jayaraman, N., Palani, Y., Jonnalagadda, R.R., and Shanmugam, E. (2022). Covalently dual functionalized graphene oxide-based multiplex electrochemical sensor for Hg (II) and Cr (VI) detection. *Sensors and Actuators B: Chemical, 367*, 132165.

Kareem, K., Rasheed, M., Liaquat, A., Hassan, A.M.M., Javed, M.I., and Asif, M. (2022). Clean energy production from jatropha plant as renewable energy source of biodiesel. *ASEAN Journal of Science and Engineering, 2*(2), 193-198.

Kaur, R., Rana, S., Singh, R., Kaur, V., and Narula, P. (2019). A Schiff base modified graphene oxide film for anodic stripping voltammetric determination of arsenite. *Microchimica Acta, 186*, 1-9.

Khan, M.S., Asif, M.I., Asif, M., Khan, M.R., Mustafa, G., and Adeel, M. (2024). Nanomaterials for the catalytic degradation and detection of microplastics: A review. *Topics in Catalysis, 66*, 1-18.

Khan, M.S., Asif, M.I., Karim, H., Zainab, S.A., Asif, M., Sohail, M., Ali, M., Munawar, J., Nawaz, S., and Haq, H.U. (2024). Electrospun fibers: promising materials for oil water separation. *Nanotechnology for Oil-Water Separation, 11*, 261-288.

Kim, E.B., Imran, M., Umar, A., Akhtar, M.S., and Ameen, S. (2022). Indandione oligomer@ graphene oxide functionalized nanocomposites for enhanced and selective detection of trace Cr2+ and Cu2+ ions. *Advanced Composites and Hybrid Materials, 5*, 1582-1594.

Kumar, R., Bhuvana, T., and Sharma, A. (2017). Nickel tungstate–graphene nanocomposite for simultaneous electrochemical detection of heavy metal ions with application to complex aqueous media*. RSC advances, 7*(67), 42146-42158.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Lee, S., Oh, J., Kim, D., and Piao, Y. (2016). A sensitive electrochemical sensor using an iron oxide/graphene composite for the simultaneous detection of heavy metal ions. *Talanta, 160*, 528-536.

Li, L., Liu, D., Shi, A., and You, T. (2018). Simultaneous stripping determination of cadmium and lead ions based on the N-doped carbon quantum dots-graphene oxide hybrid. *Sensors and Actuators B: Chemical, 255*(2), 1762-1770.

Lin, X., Lu, Z., Dai, W., Liu, B., Zhang, Y., Li, J., and Ye, J. (2018). Laser engraved nitrogen-doped graphene sensor for the simultaneous determination of Cd (II) and Pb (II). *Journal of Electroanalytical Chemistry, 828*, 41-49.

Liu, S., Wu, T., Li, F., Zhang, Q., Dong, X., and Niu, L. (2018). Disposable graphene sensor with an internal reference electrode for stripping analysis of heavy metals. *Analytical methods, 10*(17), 1986-1992.

Lu, L., Zhou, L., Chen, J., Yan, F., Liu, J., Dong, X., Xi, F., and Chen, P. (2018). Nanochannel-confined graphene quantum dots for ultrasensitive electrochemical analysis of complex samples. *ACS Nano, 12*(12), 12673-12681.

Lu, M., Deng, Y., Luo, Y., Lv, J., Li, T., Xu, J., Chen, S.W., and Wang, J. (2018). Graphene aerogel–metal–organic framework-based electrochemical method for simultaneous detection of multiple heavy-metal ions. *Analytical chemistry, 91*(1), 888-895.

Mishra, R.K., Nawaz, M.H., Hayat, A., Nawaz, M.A.H., Sharma, V., and Marty, J.L. (2017). Electrospinning of graphene-oxide onto screen printed electrodes for heavy metal biosensor. *Sensors and Actuators B: Chemical, 247*, 366-373.

Nguyen, L.D., Doan, T.C.D., Huynh, T.M., Nguyen, V.N.P., Dinh, H.H., Dang, D.M.T., and Dang, C.M. (2021). An electrochemical sensor based on polyvinyl alcohol/chitosan-thermally reduced graphene composite modified glassy carbon electrode for sensitive voltammetric detection of lead. *Sensors and Actuators B: Chemical, 345*, 130443.

Nourbakhsh, A., Rahimnejad, M., Asghary, M., and Younesi, H. (2022). Simultaneous electro-determination of trace copper, lead, and cadmium in tap water by using silver nanoparticles and graphene nanoplates as nanocomposite modified graphite electrode. *Microchemical Journal, 175*, 107137.

Pan, F., Tong, C., Wang, Z., Han, H., Pan, D., and Zhu, R. (2021). Nanocomposite based on graphene and intercalated covalent organic frameworks with hydrosulphonyl groups for electrochemical determination of heavy metal ions. *Microchimica Acta, 188*, 295.

Pang, J., Fu, H., Kong, W., Jiang, R., Ye, J., Zhao, Z., Hou, J., Sun, K., Zheng, Y., and Chen, L. (2022). Design of NiCo2O4 nanoparticles decorated N, S co-doped reduced graphene oxide composites for electrochemical simultaneous detection of trace multiple heavy metal ions and hydrogen evolution reaction. *Chemical Engineering Journal, 433*(3), 133854.

Priya, T., Dhanalakshmi, N., Thennarasu, S., Karthikeyan, V., and Thinakaran, N. (2019). Ultra sensitive electrochemical detection of Cd2+ and Pb2+ using penetrable nature of graphene/gold nanoparticles/modified L-cysteine nanocomposite. *Chemical Physics Letters, 731*, 136621.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Punrat, E., Maksuk, C., Chuanuwatanakul, S., Wonsawat, W., and Chailapakul, O. (2016). Polyaniline/graphene quantum dot-modified screen-printed carbon electrode for the rapid determination of Cr (VI) using stopped-flow analysis coupled with voltammetric technique. *Talanta, 150*, 198-205.

Rahman, M.T., Kabir, M.F., Gurung, A., Reza, K.M., Pathak, R., Ghimire, N., Baride, A., Wang, Z., Kumar, M., and Qiao, Q. (2019). Graphene oxide–silver nanowire nanocomposites for enhanced sensing of Hg2+. *ACS Applied Nano Materials, 2*(8), 4842-4851.

Rehman, A.U., Fayaz, M., Lv, H., Liu, Y., Zhang, J., Wang, Y., Du, L., Wang, R., and Shi, K. (2022). Controllable synthesis of a porous PEI-functionalized Co3O4/rGO nanocomposite as an electrochemical sensor for simultaneous as well as individual detection of heavy metal ions. *ACS omega, 7*(7), 5870-5882.

Saisree, S., Nair, A.J.S., and Yesodha, S.K. (2023). Graphene quantum dots doped with sulfur and nitrogen as versatile electrochemical sensors for heavy metal ions Cd(II), Pb(II), and Hg(II). *ACS Applied Nano Materials, 6*(2), 1224-1234.

Shi, L., Li, Y., Rong, X., Wang, Y., and Ding, S. (2017). Facile fabrication of a novel 3D graphene framework/Bi nanoparticle film for ultrasensitive electrochemical assays of heavy metal ions. *Analytica chimica acta, 968*, 21-29.

Si, Y., Liu, J., Chen, Y., Miao, X., Ye, F., Liu, Z., and Li, J. (2018). rGO/AuNPs/tetraphenylporphyrin nanoconjugate-based electrochemical sensor for highly sensitive detection of cadmium ions. *Analytical Methods, 10*(29), 3631-3636.

Soman, S., Aswathy, P.V., and Kala, R. (2021). Covalently modified graphene quantum dot using a thiourea based imprinted polymer for the selective electrochemical sensing of Hg (II) ions. Journal of Polymer Research, 2021. 28(9): p. 359.

Srivastava, M., Srivastava, A., and Pandey, S.K. (2020). Suitability of graphene monolayer as sensor for carcinogenic heavy metals in water: A DFT investigation. *Applied Surface Science, 517*, 146021.

Teodoro, K.B.R., Migliorini, F.L., Facure, M.H.M., and Correa, D.S. (2019). Conductive electrospun nanofibers containing cellulose nanowhiskers and reduced graphene oxide for the electrochemical detection of mercury (II). *Carbohydrate polymers, 207*, 747-754.

Thiruppathi, A.R., Sidhureddy, B., Keeler, W., and Chen, A. (2017). Facile one-pot synthesis of fluorinated graphene oxide for electrochemical sensing of heavy metal ions. *Electrochemistry Communications, 76*, 42-46.

Tian, B., Kou, Y., Jiang, X., Lu, J., Xue, Y., Wang, M., and Tan, L. (2020). Ultrasensitive determination of mercury ions using a glassy carbon electrode modified with nanocomposites consisting of conductive polymer and amino-functionalized graphene quantum dots. *Microchimica Acta, 187*, 1-12.

Vajedi, F., and Dehghani, H. (2019). The characterization of TiO2-reduced graphene oxide nanocomposites and their performance in electrochemical determination for removing heavy metals ions of cadmium (II), lead (II) and copper (II). *Materials Science and Engineering: B, 243*, 189-198.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Wei, P., Zhu, Z., Song, R., Li, Z., and Chen, C. (2019). An ion-imprinted sensor based on chitosan-graphene oxide composite polymer modified glassy carbon electrode for environmental sensing application. *Electrochimica Acta, 317*, 93-101.

Wu, W., Jia, M., Wang, Z., Zhang, W., Zhang, Q., Liu, G., Zhang, Z., and Li, P. (2019). Simultaneous voltammetric determination of cadmium(II), lead(II), mercury(II), zinc(II), and copper(II) using a glassy carbon electrode modified with magnetite (Fe3O4) nanoparticles and fluorinated multiwalled carbon nanotubes. *Microchimica Acta,* 186, 97.

Xu, X., Lv, X., Tan, F., Li, Y., Geng, C., Cui, B., and Fang, Y. (2021). Simultaneous electrochemical detection of multiple heavy-metal ions based on furfural/reduced graphene oxide composites. *Journal of The Electrochemical Society, 168*(12), 126516.

Xu, Y., Zhang, W., Huang, X., Shi, J., Zou, X., Li, Z., and Cui, X. (2019). Adsorptive stripping voltammetry determination of hexavalent chromium by a pyridine functionalized gold nanoparticles/three-dimensional graphene electrode. *Microchemical Journal, 149*, 104022.

Xuan, X., Hossain, M.D.F., and Park, J.Y. (2016). Solvothermal-assisted, reduced-graphene-oxide-modified bismuth electrode for an electrochemical heavy-metal-ion sensor. *Journal of Nanoscience and Nanotechnology, 16*(11), 11421-11424.

Yi, W., He, Z., Fei, J., and He, X. (2019). Sensitive electrochemical sensor based on poly (L-glutamic acid)/graphene oxide composite material for simultaneous detection of heavy metal ions. *RSC advances, 9*(30), 17325-17334.

Yousuf, S., A. Donald, A.N., Hassan, A.M.M., Iqbal, A., Bodlah, M.A., Sharf, B., Noshia, N., and Asif, M. (2022). A review on particulate matter and heavy metal emissions; impacts on the environment, detection techniques and control strategies. *MOJ Ecology & Environmental Sciences, 7*(1), 1-5.

Zhang, Y., Liu, M., Pan, S., Yu, L., Zhang, S., and Liu, R. (2022). A magnetically induced self-assembled and label-free electrochemical aptasensor based on magnetic Fe3O4/Fe2O3@ Au nanoparticles for VEGF165 protein detection. *Applied Surface Science, 580*, 152362.

Zhao, G., Wang, H., Liu, G., Wang, Z., and Cheng, J. (2017). Simultaneous determination of trace Cd (II) and Pb (II) based on Bi/Nafion/reduced graphene oxide-gold nanoparticle nanocomposite film-modified glassy carbon electrode by one-step electrodeposition. *Ionics, 23*, 767-777.

Zhao, Q., Xu, X., Xu, Y., Gongsun, K., Hu, L., Yan, S., Yao, W., and Yan, Z. (2020). Synergistically improved electrochemical performance and its practical application of graphene oxide stabilized nano Ag2S by one-pot homogeneous precipitation. *Applied Surface Science, 501*, 144208.

Zhu, H., Xu, Y., Liu, A., Kong, N., Shan, F., Yang, W., Barrow, C.J., and Liu, J. (2015). Graphene nanodots-encaged porous gold electrode fabricated via ion beam sputtering deposition for electrochemical analysis of heavy metal ions. *Sensors and Actuators B: Chemical, 206*, 592-600.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951

Zhu, L., Xu, L., Huang, B., Jia, N., Tan, L., and Yao, S. (2014). Simultaneous determination of Cd (II) and Pb (II) using square wave anodic stripping voltammetry at a gold nanoparticle-graphene-cysteine composite modified bismuth film electrode. *Electrochimica Acta, 115*, 471-477.

Zuo, Y., Xu, J., Zhu. X., Duan. X., Lu, L., and Yu, Y. (2019). Graphene-derived nanomaterials as recognition elements for electrochemical determination of heavy metal ions: A review. *Microchimica Acta, 186*, 1-17.

DOI:
p-ISSN: 2828-920X e-ISSN: 2828-9951